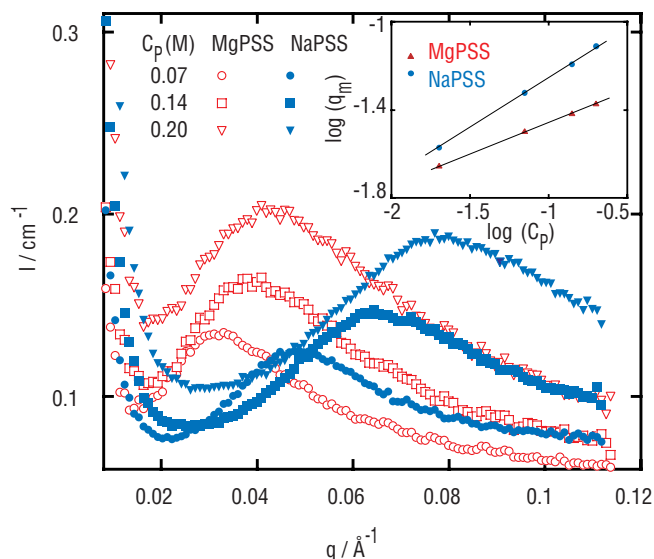


# DIMENSIONS OF POLYELECTROLYTE CHAINS WITH MULTIVALENT COUNTERIONS

**P**olyelectrolytes, macromolecules carrying a large number of charges, are the predominant water-soluble synthetic and natural polymers. They have wide industrial application and critical biological function. For industry, polyelectrolytes are used as stabilizers, flocculants, or surface-active agents for water treatment, paper, paints, personal care products, and pharmaceuticals. In biological systems, the binding of proteins and nucleic acids, the functioning of enzymes, and the construction of cellular components are controlled by the tensions imposed by electrostatic interactions. It is also clear that the interaction of polyelectrolytes with multivalent counterions is a critical factor in many industrial applications and biological functions. Although recent years have witnessed an impressive confluence of experiments, simulations, and theory, long-range electrostatic interactions still disrupt most traditional methods and characterization techniques. In the work described here, the method of zero-average-contrast small angle neutron scattering (SANS) is used to overcome this barrier and probe directly the most fundamental polymer property, the chain dimension, as a function of concentration and counterion valence.

For low ionic strength polyelectrolyte solutions SANS shows a maximum at finite wavevector and a steep upturn at low angles; results that are dramatically different from those of neutral polymer solutions[1]. There is no complete theory, only qualitative descriptions for these phenomena that appear for nearly all charged macromolecules. The situation is even more complicated for typical biological systems or for commercial polyelectrolyte applications because of the presence of divalent or trivalent counterions. The specificity of interactions with multivalent ions is critical to applications such as water treatment and to biological processes such as protein folding and DNA packing. Although the multivalent counterions have dramatic effects on the structure and dynamics of polyelectrolyte solutions, experimental work with scattering is both limited and difficult to interpret. A major impediment for simulations and theoretical interpretation is the lack of an adequate description for the single chain structure and dimension. The overwhelming effect of strong intramolecular and intermolecular electrostatic interactions of the unscreened charges dominates the scattering, even in dilute solution.

The method of zero-average-contrast (ZAC) in small angle neutron scattering provides a means to overcome this obstacle and to measure single chain dimensions in dilute and semidilute

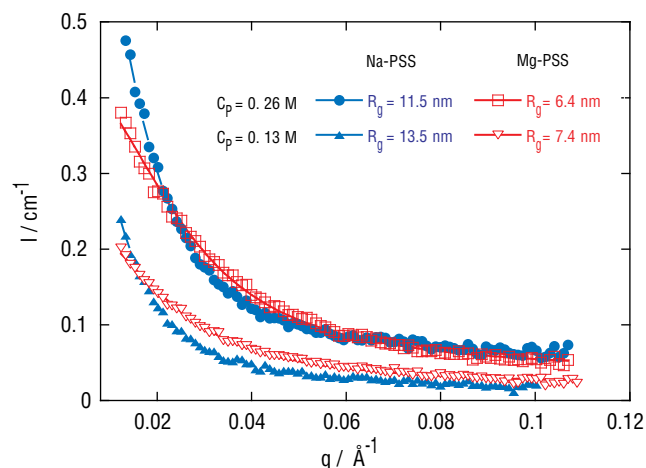


**FIGURE 1. Full contrast SANS for NaPSS (filled) and MgPSS (unfilled) in  $\text{D}_2\text{O}$ . Monomer concentrations: ( $\nabla$ ) 0.20 mol/L, ( $\blacksquare$ ) 0.14 mol/L, and ( $\bullet$ ) 0.07 mol/L. Inset is log-log plot of peak position versus monomer concentration.**

solutions[2]. The ZAC method requires matched pairs of deuterated and hydrogenated polymers and a specific H-D solvent composition, but the charge concentration and counterions can be changed over a broad range.

Poly(styrene sulfonate) (PSS) with matched degree of polymerization and degree of sulfonation was obtained as deuterated PSS and hydrogenated PSS. The sodium salt of PSS was purified by ion-exchange, dialysis, neutralization titration with NaOH or  $\text{Mg}(\text{OH})_2$ , and lyophilization. Figure 1 shows typical polyelectrolyte scattering (performed on the NG1 8 m SANS instrument) in  $\text{D}_2\text{O}$  without added salt. Although qualitatively the two sets are similar, including strong upturns at low  $q$ , the concentration dependence of the broad maxima is shown in the inset with  $q_{\text{max}} \propto c_p^{0.46}$  for NaPSS and  $c_p^{0.29}$  for MgPSS, where  $c_p$  is the monomer concentration. Peaks for the divalent counterion polymer are also shifted to lower  $q$ .

All of these features disappear under the zero-average-contrast conditions. ZAC is achieved with an equimolar mixture of deuterated and hydrogenated polymer in a mixture of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The fraction of  $\text{D}_2\text{O}$  in the solution is set at the value necessary to satisfy the “optical theta condition,” where the scattering length densities of the hydrogenated and deuterated

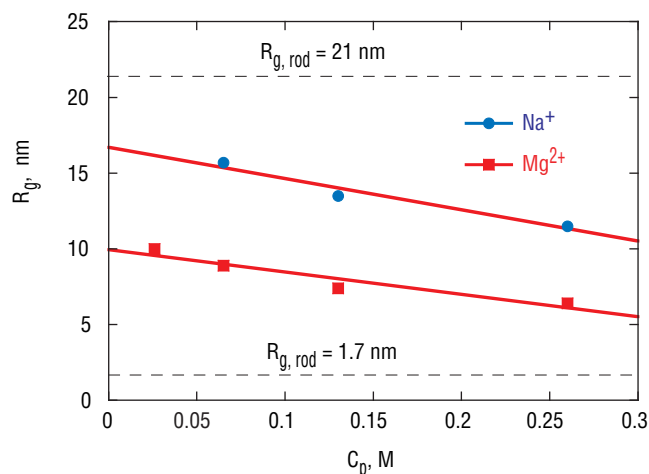


**FIGURE 2.** ZAC scattering from Na and Mg polyelectrolyte solutions under conditions of zero average contrast showing single chain scattering. Fits are to the Debye function.

monomers are equal and opposite. Figure 2 displays the scattering profiles from the ZAC solutions for NaPSS and MgPSS. Each decreases monotonically with angle, as expected for the intraparticle scattering function, and each is fit adequately with a Debye function.

Figure 3 shows the values of polymer chain radius of gyration as a function of concentration for NaPSS and MgPSS along with calculated estimates for the size of a single chain with degree of polymerization of 300 under random coil and rod-like configurations. For both systems, the chain dimension decreases with increasing concentration with the MgPSS chains nearly a factor of two smaller for each concentration. While the monovalent counterion chains are highly extended, they are not at the rod-like limit. At the same time, both systems are more expanded than the calculated ideal Gaussian chain value. This result implies that while the divalent counterions induce a coil contraction they do not produce a coil collapse or a coil-globule transition.

This study demonstrates the power of the zero-average-contrast method to extract single chain information even in the presence of strong intermolecular interactions. The method, here used for dilute low ionic strength solutions, has also been applied to measure single chain dimensions in solutions at high concentration and with arbitrary amounts of added salts as needed to explore the range of real conditions important for polyelectrolytes.



**FIGURE 3.** Polyelectrolyte chain dimensions as a function of concentration with comparison to model chain calculations.

## REFERENCES

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